

## DESCRIPTION

### **CARBON NANOTUBE COMPOSITE ELECTRODE CAPACITOR HAVING SUPER HIGH CAPACITANCE AND FABRICATION METHOD THEREOF**

The present invention relates to a carbon nanotube composite electrode capacitor with super high capacitance and a method for fabricating the same, and pertains to the fields of nanotechnology and energy storage.

The capacitor with super high capacitance is a novel energy storage element between the storage battery and the capacitor of conventional medium. The capacitor of conventional medium stores electric charge by polarization of the dielectric medium, while the capacitor with super high capacitance stores electric charge by interaction between electrolytic ions and electrodes. In comparison with the capacitor of conventional medium, the capacitor with super high capacitance has very high specific capacitance, and the density of the energy storable thereby is over ten times higher than that storable by the capacitor of conventional medium; in comparison with the storage battery, the capacitor with super high capacitance has higher power density of over ten times, and possesses the characteristics of instantaneously releasing extremely high electric currents, of high efficiency in charging and long life of recycled use.

The capacitor with super high capacitance can be used as the power unit of the driving power for an electrically driven automobile, thus solving the "bottleneck" restricting the development of electrically driven vehicles. The electrically driven automobile having a composite driving power of the storage battery and the capacitor with super high capacitance is supplied by the storage battery with the average power required under the normal operation state, while it is supplied by the capacitor with super high capacitance with the acceleration power required under the states of climbing, starting and braking. As a "peak value power unit", the capacitor with super high capacitance can effectively reduce the peak value power pressure of the storage battery, enhance for several times the sustained mileage of each charge of the storage battery, and prolong the life of recycled use of the storage battery. The capacitor with super high capacitance can also find applications in the military field, for instance, by providing extremely high start power of the MW magnitude for microwave weaponry and laser weaponry, applications in electronic apparatuses as standby power sources, for instance, by serving as uninterrupted power supply system for televisions, camcorders, personal computers and mobile phones, and applications in flashing and igniting

devices for industrial equipments, for instance, by serving as initiating power sources for cameras, electric welders, magnetizing apparatuses, roentgen machines, and fuel cells.

The capacitance formation mode of the capacitor with super high capacitance is divided into two kinds of an electric double-layer capacitance and a pseudodielectric capacitance, of which the electric double-layer capacitance is formed by opposition of electric charges due to orientated arrangement of electrons and ions at the electrode/electrolyte interface, and of which the pseudodielectric capacitance is thus formed, that electrically active substances generate highly reversible oxidation-reduction reaction or absorption/desorption process at the two-dimensional or quasi-two-dimensional space on the surface or in the bulk of the electrode to thereby achieve storage and release of electric charges. The specific capacitance formed by means of the pseudodielectric capacitance mode is over ten times as high as that formed by the electric double-layer capacitance mode. The devices that correspond to the aforementioned two capacitance modes are the electric double-layer capacitor and the pseudodielectric capacitor.

Usually, the electric double-layer capacitor mainly employs active carbons, active carbon fibers and carbon aerosols with large specific surface areas as the materials of the electrode, but these materials have inferior conductivity, so that the equivalent series resistance of the capacitor as obtained is large. In addition, since the active carbons contain great quantities of minute apertures having an aperture ratio of 2nm or less, it is difficult for the electrolytic ions to enter these apertures, and consequently the utilization ratio of the specific surface area is low; moreover, there are so-called "dead apertures" in the structure, so that the frequency response characteristics are inferior. With the discovery of carbon nanotubes in recent years, application of the carbon nanotubes as the material for the electrode of the capacitor with super high capacitance has caught more and more attention of researchers. Carbon nanotubes are hollow and tubular material of nano grade formed by curling of single-layered or multiple-layered graphite surfaces. Under certain conditions of shape and size, carbon nanotubes have good conductivity. Carbon nanotubes interweave and interwind one another to form a netlike structure, with the sizes of the net apertures being mainly distributed at a range between 2-50 nm, and with a very large effective specific surface area suitable for formation of the electric double-layer capacitance. The net apertures of the three-dimensional network of the carbon nanotubes run through one another, and there are no so-called "dead apertures" in the structure of the active carbons. However, the carbon nanotubes are mainly employed to form the electric double-layer capacitance having relatively small specific capacitance of approximately 100 F/g (calculated in terms of single-electrode active

substances). Refer, for instance, to *Super Capacitor Based on Carbon Nanotubes* by Renzhi MA, Bingqing WEI and Cailu XU et al., published in the magazine *Sciences in China* (Edition E, 2000, 30(2): 112-116).

In contrast, the pseudodielectric capacitor usually employs metal oxide  $\text{RuO}_2$  as the material of the electrode, as the  $\text{RuO}_2$  has high conductivity, and the capacitor with super high capacitance obtained thereby has high specific capacitance. But the  $\text{RuO}_2$  is expensive, and the search for inexpensive electrode material to replace the  $\text{RuO}_2$  has roused interests of researchers, see for instance, *Research on Super Capacitors with Nickel Oxide* by Xiaofeng WANG et al., published in the magazine *Power Source Technology* (2001, 25(3)). The oxide of nickel ( $\text{NiO}_x$ ) is used as the material of the electrode, but the oxide of nickel ( $\text{NiO}_x$ ) has inferior conductivity, so that the equivalent series resistance of the capacitor with super high capacitance as obtained is large. In addition, the formability of transition metal oxides is bad. Another kind of electrode material of the pseudodielectric capacitor is conducting polymers, including polyaminobenzene (PAN) and its derivatives, polythiophene (PTH) and its derivatives, polypyrrole (PPY) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives. The capacitor with super high capacitance based on conducting polymers can form pseudodielectric capacitance and hence acquire a relatively large specific capacitance, but the conductivity of the conducting polymers is also inferior. Additionally, the mechanical robustness of the conducting polymers is low.

The material of the electrode decides the performance of the capacitor with super high capacitance. The carbon nanotube amongst the previously mentioned electrode materials can achieve relatively high conductivity, but it is mainly used to form the electric double-layer capacitance having relatively small specific capacitance. By contrast, the transition metal oxides and the conducting polymers can form the pseudodielectric capacitance and achieve relatively higher specific capacitance but inferior conductivity. This means that the currently available electrode materials of the capacitor with super high capacitance cannot put emphasis simultaneously on the high specific capacitance and on the high conductivity. Moreover, the formability of the transition metal oxides is inferior, and the conducting polymers have low mechanical robustness. All these affect the performance of the capacitor with super high capacitance.

In the patent for invention, entitled *Carbon-Doped Nanotube Capacitor with Super High Capacitance*, applied by Xutao FU and others, and application numbered 00136008. 6, active carbons (or active carbon fibers) are compounded with carbon nanotubes to serve as the electrode material of the capacitor with super high capacitance, but this material does not contain any transition metal oxide or conducting polymer, so that it is difficult to form the

pseudodielectric capacitance, and that the specific capacitance as obtained is small. In the patent for invention, entitled Super Capacitor Having Electrode of New Material and Fabrication Method thereof, applied by Yongxi LI and others, and application numbered 01109703. 5, carbon nanotubes or nickel-plated carbon nanotubes are used as electrode material of an ion capacitor with super high capacitance, but this material does not contain any transition metal oxide or conducting polymer, so that it is difficult to form the pseudodielectric capacitance; in addition, the cost of this material is too high. Finally in the patent for invention, entitled Electrochemical Super Capacitor and Fabrication Method thereof, applied by Jingying XIE and others, and application numbered 00119499. 2, the oxide of nickel or hydroxide is used as the material of the positive electrode of an ion capacitor with super high capacitance, and porous large-area carbons are used as the material of the negative electrode, but the oxide of nickel or hydroxide has inferior conductivity, so that the equivalent series resistance of the capacitor with super high capacitance as obtained thereby is large.

The objectives of the present patent for invention are to obtain an electrode material of a capacitor with super high capacitance capable of simultaneously forming high specific capacitance, having good conductivity, good formability and good mechanical performance, to obtain an electrode fabricated thereby, and to fabricate a capacitor with super high capacitance having high specific capacitance and low equivalent series resistance.

The principle of the present patent for invention is described below. An approach is proposed to compound carbon nanotubes with transition metal oxides and/or conducting polymers, the carbon nanotubes of the composite electrode obtained thereby have good conductivity, and the transition metal oxides and the conducting polymers can form relatively high specific capacitance. The carbon nanotubes in the composite electrode form a netlike structure, which becomes an electric charge passage with good conductivity, while the transition metal oxides and the conducting polymers can form pseudodielectric capacitance to obtain relatively high specific capacitance, thereby making it possible that the electrode of the capacitor with super high capacitance can not only form high specific capacitance but also possess high conductivity. In addition, in the material of the carbon nanotubes composite electrode, the specific surface area of the carbon nanotubes themselves is large, thereby making it possible to form relatively high electric double-layer capacitance; during the process of preparing the composite material, the carbon nanotubes can serve as a nucleation substrate for the transition metal oxides and the conducting polymers, thus facilitating acquisition of transition metal oxides and conducting polymers with minute grain size; moreover, the carbon nanotubes, the transition metal oxides and the conducting polymers are complementary in terms of their mechanical performance, for instance, the

transition metal oxides can be adsorbed on the network of the carbon nanotubes to thereby acquire good formability; the conducting polymers have inferior mechanical robustness, but their compounding with the carbon nanotubes markedly enhances their mechanical robustness. As should be noted, formability and mechanical robustness are also of very great importance to the electrode materials.

The technical solution for the essential technical problem of the present patent for invention is achieved thus, that the present patent for invention makes use of a method for compounding carbon nanotubes having good conductivity with other transition metal oxides, conducting polymer series and active carbon series having inferior conductivity as dealt with, to thereby obtain an electrode material of a capacitor with super high capacitance capable of simultaneously forming high specific capacitance and having good conductivity. There are six specific compounding solutions as described below.

- (1) Compounding of the carbon nanotubes with the transition metal oxides: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, and the transition metal oxides occupy 90%-10% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ).
- (2) Compounding of the carbon nanotubes with the conducting polymer series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, and the conducting polymers occupy 90%-10% by wt. percent; wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives.
- (3) Compounding of the carbon nanotubes simultaneously with the transition metal oxides and the conducting polymers: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 50%-5% by wt. percent, and the conducting polymers occupy 40%-5% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), and wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives.
- (4) Compounding of the carbon nanotubes simultaneously with the transition metal oxides and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal

oxides occupy 50%-5% by wt. percent, and the active carbon series occupies 40%-5% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.

- (5) Compounding of the carbon nanotubes simultaneously with the conducting polymer series and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the conducting polymers occupy 50%-5% by wt. percent, and the active carbon series occupies 40%-5% by wt. percent; wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives, and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.
- (6) Compounding of the carbon nanotubes simultaneously with the transition metal oxides, the conducting polymers and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 30%-3% by wt. percent, the conducting polymers occupy 30%-5% by wt. percent, and the active carbon series occupies 30%-2% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives, and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.

The carbon nanotubes in the aforementioned six compounding solutions should be performed with an oxidation process before compounding. The oxidation process is carried out in the air or in a liquid medium under a temperature range of 80-120°C for 2-10 hours. The transition metal oxides in the aforementioned solutions can be either doped with a rare earth element Ce or La, or not doped with the rare earth element Ce or La. Subsequently, the material is prepared in accordance with the compounding solutions, sufficient grinding is performed, and a binder of 1%-20% by wt. percent is then added thereto, which binder includes teflon emulsion, carboxymethyl cellulose, and polyvinyl alcohol. The evenly churned composite electrode material is pressed onto foamed nickel, graphite sheet, nickel sheet, aluminum sheet or copper sheet to fabricate a composite electrode having a predetermined shape. The pressing method includes common die pressing, cold isostatic pressing and

hot isostatic pressing. Two identical carbon nanotube composite electrodes are separated by a diaphragm passable by electrolytic ions, which diaphragm is all-glass paper or a polymeric membrane. The same is then encapsulated in an outer housing into which is then injected an electrolytic solution, which can be a sodium hydroxide aqueous solution, a potassium hydroxide aqueous solution, a lithium hydroxide aqueous solution, a sulfuric aqueous solution, a nitric acid aqueous solution, a propylene carbonate solution of lithium perchlorate, a propylene carbonate solution of benzyltriethylammonium tetrafluoroborate, or a solution of mixtures thereof. The final product after the encapsulation is the capacitor with super high capacitance.

Embodiments: the existing electrode materials of the capacitor with super high capacitance as dealt with in the present invention can be divided into two kinds, one of which is carbon nanotubes having good conductivity, and another one of which is transition metal oxides, active carbon series and conducting polymer series. The present invention makes use of a method for compounding carbon nanotubes having good conductivity with other transition metal oxides, active carbon series and conducting polymer series having inferior conductivity as dealt with, to thereby obtain an electrode material of a capacitor with super high capacitance capable of simultaneously forming high specific capacitance and having good conductivity. There are six specific compounding solutions as described below.

- (1) Compounding of the carbon nanotubes with the transition metal oxides: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, and the transition metal oxides occupy 90%-10% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ).
- (2) Compounding of the carbon nanotubes with the conducting polymer series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, and the conducting polymers occupy 90%-10% by wt. percent; wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives.
- (3) Compounding of the carbon nanotubes simultaneously with the transition metal oxides and the conducting polymers: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 50%-5% by wt. percent, and the conducting polymers occupy 40%-5% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), and wherein the conducting polymer series includes polyaminobenzene (PAN) and its

derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives.

- (4) Compounding of the carbon nanotubes simultaneously with the transition metal oxides and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 50%-5% by wt. percent, and the active carbon series occupies 40%-5% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.
- (5) Compounding of the carbon nanotubes simultaneously with the conducting polymer series and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the conducting polymers occupy 50%-5% by wt. percent, and the active carbon series occupies 40%-5% by wt. percent; wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives, and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.
- (6) Compounding of the carbon nanotubes simultaneously with the transition metal oxides, the conducting polymers and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 30%-3% by wt. percent, the conducting polymers occupy 30%-5% by wt. percent, and the active carbon series occupies 30%-2% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives, and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.

The carbon nanotubes in the aforementioned six compounding solutions should be performed with an oxidation process before compounding. The oxidation process is carried out in the air or in a liquid medium under a temperature range of 80-120°C for 2-10 hours. The transition metal oxides in the aforementioned solutions can be either doped with a rare earth element Ce or La, or not doped with the rare earth element Ce or La. Subsequently, the



material is prepared in accordance with the compounding solutions, sufficient grinding is performed, and a binder of 1%-20% by wt. percent is then added thereto, which binder includes teflon emulsion, carboxymethyl cellulose, and polyvinyl alcohol. The evenly churned composite electrode material is pressed onto foamed nickel, graphite sheet, nickel sheet, aluminum sheet or copper sheet to fabricate a composite electrode having a predetermined shape. The pressing method includes common die pressing, cold isostatic pressing and hot isostatic pressing. Two identical carbon nanotube composite electrodes are separated by a diaphragm passable by electrolytic ions, which diaphragm is all-glass paper or a polymeric membrane. The same is then encapsulated in an outer housing into which is then injected an electrolytic solution, which can be a sodium hydroxide aqueous solution, a potassium hydroxide aqueous solution, a lithium hydroxide aqueous solution, a sulfuric aqueous solution, a nitric acid aqueous solution, a propylene carbonate solution of lithium perchlorate, a propylene carbonate solution of benzyltriethylammonium tetrafluoroborate, or a solution of mixtures thereof. The final product after the encapsulation is the capacitor with super high capacitance.

The advantages of the present patent for invention are described below. The carbon nanotubes in the aforementioned composite electrode can form a conductive network having good conductivity, while the transition metal oxides and the conducting polymer series therein can form high specific capacitance. It is thus possible to obtain an electrode material of a capacitor with super high capacitance capable of simultaneously forming high specific capacitance and having good conductivity. In addition, in the material of the carbon nanotubes composite electrode, the specific surface area of the carbon nanotubes themselves is large, thereby making it possible to form relatively high electric double-layer capacitance; during the process of preparing the composite material, the carbon nanotubes can serve as a nucleation substrate for the transition metal oxides and the conducting polymers, thus facilitating acquisition of transition metal oxides and conducting polymers with minute grain size; moreover, the carbon nanotubes, the transition metal oxides and the conducting polymers are complementary in terms of their mechanical performance, for instance, the transition metal oxides can be adsorbed on the network of the carbon nanotubes to thereby acquire good formability; the conducting polymers have inferior mechanical robustness, but their compounding with the carbon nanotubes markedly enhances their mechanical robustness; furthermore, the addition of the active carbon series can lower the production cost. Application of the present patent indicates the appearance of a novel electrode material of a capacitor with super high capacitance, and this will advance the application and research progresses of capacitors with super high capacitance, and give rise to great economic and social benefits. It is possible, through implementation of the present invention, to obtain an electrode material of a capacitor with super high capacitance capable of

simultaneously forming high specific capacitance; having good conductivity, good formability and good mechanical performance; and the use of this electrode material makes it possible to fabricate capacitors with super high capacitance.

## CLAIMS

1. The present invention relates to a carbon nanotube composite electrode capacitor with super high capacitance and a method for fabricating the same, whereby carbon nanotubes having good conductivity are compounded with transition metal oxides, conducting polymer series and active carbon series having inferior conductivity as dealt with; characterized in that there are six specific compounding solutions as follows:
  - (1) compounding of the carbon nanotubes with the transition metal oxides: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, and the transition metal oxides occupy 90%-10% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ );
  - (2) compounding of the carbon nanotubes with the conducting polymer series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, and the conducting polymers occupy 90%-10% by wt. percent; wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives;
  - (3) compounding of the carbon nanotubes simultaneously with the transition metal oxides and the conducting polymers: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 50%-5% by wt. percent, and the conducting polymers occupy 40%-5% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), and wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives;
  - (4) compounding of the carbon nanotubes simultaneously with the transition metal oxides and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 50%-5% by wt. percent, and the active carbon series occupies 40%-5% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols;

- (5) compounding of the carbon nanotubes simultaneously with the conducting polymer series and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the conducting polymers occupy 50%-5% by wt. percent, and the active carbon series occupies 40%-5% by wt. percent; wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives, and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols; and
  - (6) compounding of the carbon nanotubes simultaneously with the transition metal oxides, the conducting polymers and the active carbon series: in this compound material the carbon nanotubes occupy 10%-90% by wt. percent, the transition metal oxides occupy 30%-3% by wt. percent, the conducting polymers occupy 30%-5% by wt. percent, and the active carbon series occupies 30%-2% by wt. percent; wherein the transition metal oxides include the oxide of nickel ( $\text{NiO}_x$ ) and the oxide of cobalt ( $\text{CoO}_x$ ), wherein the conducting polymer series includes polyaminobenzene (PAN) and its derivatives, polypyrrole (PPY) and its derivatives, polythiophene (PTH) and its derivatives, polyparaphenylene (PPP) and its derivatives, and polyacene (PAS) and its derivatives, and wherein the active carbon series includes active carbons, active carbon fibers, active carbon fiber cloths, and carbon aerosols.
2. The carbon nanotube composite electrode capacitor with super high capacitance and the method for fabricating the same according to claim 1, characterized in that the carbon nanotubes in said six compounding solutions is performed with an oxidation process before compounding, wherein the oxidation process is carried out in the air or in a liquid medium under a temperature range of 80-120°C for 2-10 hours.
  3. The carbon nanotube composite electrode capacitor with super high capacitance and the method for fabricating the same according to claim 1, characterized in that the transition metal oxides in said solutions can be either doped with a rare earth element Ce or La, or not doped with the rare earth element Ce or La.
  4. The carbon nanotube composite electrode capacitor with super high capacitance and the method for fabricating the same according to claim 1, characterized in that the material is prepared in accordance with the compounding solutions, that sufficient grinding is performed, and that a binder of 1%-20% by wt. percent is then added thereto, wherein the binder includes teflon emulsion, carboxymethyl cellulose, and polyvinyl alcohol.

5. The carbon nanotube composite electrode capacitor with super high capacitance and the method for fabricating the same according to claim 1, characterized in that evenly churned composite electrode material is pressed onto foamed nickel, graphite sheet, nickel sheet, aluminum sheet or copper sheet to fabricate a composite electrode having a predetermined shape.
6. The carbon nanotube composite electrode capacitor with super high capacitance and the method for fabricating the same according to claim 1, characterized in that a pressing method includes die pressing, cold isostatic pressing and hot isostatic pressing.

## **ABSTRACT**

The present invention is intended to propose an approach to compound carbon nanotubes with transition metal oxides and/or conducting polymers. The carbon nanotubes have good conductivity, form in a composite electrode a netlike structure, which becomes an electric charge passage with good conductivity, while the transition metal oxides and the conducting polymers can form pseudodielectric capacitance to obtain relatively high specific capacitance, thereby making it possible that the electrode of the capacitor with super high capacitance can not only form high specific capacitance but also possess high conductivity. In addition, the specific surface area of the carbon nanotubes in the composite electrode is large, thereby making it possible to form relatively high electric double-layer capacitance; during the process of preparation, the carbon nanotubes can serve as a nucleation substrate for the transition metal oxides and the conducting polymers, thus facilitating acquisition of transition metal oxides and conducting polymers with minute grain size; compounding of the carbon nanotubes with the transition metal oxides and the conducting polymers makes it possible to obtain good formability and high mechanical robustness.

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[54]发明名称 碳纳米管复合电极超大容量电容器及其制造方法

[57]摘要

本发明拟采用碳纳米管与过渡金属氧化物与(或)导电聚合物相复合的途径。碳纳米管具有良好的导电性,在复合电极中形成网状结构,成为导电性良好的电荷通路;而过渡金属氧化物、导电聚合物能形成赝电容、得到较高的比电容量,这使得超大容量电容器电极既能形成高比电容量、又具有高电导率。另外,复合电极中的碳纳米管比表面积大,可以形成较大的双电层容量;碳纳米管可在制备过程作为过渡金属氧化物、导电聚合物的形核基底,有利于得到晶粒细小的过渡金属氧化物、导电聚合物;碳纳米管与过渡金属氧化物、导电聚合物复合,可得到较好的成型性能和较高地机械强度。

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1、 本发明涉及一种碳纳米管复合电极超大容量电容器及其制造方法,采用将导电性良好的碳纳米管与涉及到的导电性较差的过渡金属氧化物、导电聚合物系列、活性炭系列相复合,其特征在于具体的复合方案有如下6种:

(1) 碳纳米管与过渡金属氧化物复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,过渡金属氧化物的重量百分比为 90%-10%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )。

(2) 碳纳米管与导电聚合物系列复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,导电聚合物的重量百分比为 90%-10%。这里的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物。

(3) 碳纳米管与过渡金属氧化物、导电聚合物同时复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,过渡金属氧化物的重量百分比为 50%-5%,导电聚合物的重量百分比为 40%-5%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )；这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物。

(4) 碳纳米管与过渡金属氧化物、活性炭系列同时复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,过渡金属氧化物的重量百分比为 50%-5%,活性炭系列的重量百分比为 40%-5%。这里所指的过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )；这里所指的活性炭



系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。

(5) 碳纳米管与导电聚合物系列、活性炭系列同时复合, 这一复合材料中碳纳米管的重量百分比为 10%-90%, 导电聚合物的重量百分比为 50%-5%, 活性炭系列的重量百分比为 40%-5%。这里所指的导电聚合物系列包括聚苯胺 (PAN) 及其衍生物、聚吡咯 (PPY) 及其衍生物、聚噻吩 (PTH) 及其衍生物、聚对苯 (PPP) 及其衍生物、聚并苯 (PAS) 及其衍生物; 这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。

(6) 碳纳米管与过渡金属氧化物、导电聚合物、活性炭系列同时复合, 这一复合材料中碳纳米管的重量百分比为 10%-90%, 过渡金属氧化物的重量百分比为 30%-3%, 导电聚合物的重量百分比为 30%-5%, 活性炭系列的重量百分比为 30%-2%。这里所指过渡金属氧化物包括镍的氧化物 ( $\text{NiO}_x$ )、钴的氧化物 ( $\text{CoO}_x$ ); 这里所指的导电聚合物系列包括聚苯胺 (PAN) 及其衍生物、聚吡咯 (PPY) 及其衍生物、聚噻吩 (PTH) 及其衍生物、聚对苯 (PPP) 及其衍生物、聚并苯 (PAS) 及其衍生物; 这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。

2、 根据权利要求 1 所述的碳纳米管复合电极超大容量电容器及其制造方法, 其特征在于上述 6 种复合方案中所提到的碳纳米管在复合前需进行氧化处理, 氧化处理在空气或液体介质中进行, 氧化处理温度为 80-120℃, 氧化处理时间为 2-10 小时。

3、 根据权利要求 1 所述的碳纳米管复合电极超大容量电容器及其制造方法,

其特征在于上述方案中提到的过渡金属氧化物中可以掺入稀土元素 Ce 或 La; 也可以不掺 Ce 或 La。

- 4、 根据权利要求 1 所述的碳纳米管复合电极超大容量电容器及其制造方法, 其特征在于按复合方案配料, 进行充分研磨, 再在其中加入重量百分比为 1%-20%的粘结剂, 粘结剂包括聚四氟乙烯乳液、羧甲基纤维素、聚乙烯醇。
- 5、 根据权利要求 1 所述的碳纳米管复合电极超大容量电容器及其制造方法, 其特征在于用搅拌均匀的复合电极材料压制在泡沫镍、石墨片、镍片、铝片或铜片上, 制成一定形状的复合电极。
- 6、 根据权利要求 1 所述的碳纳米管复合电极超大容量电容器及其制造方法, 其特征在于压制方法包括模压法、冷等静压法、热等静压法。

## 碳纳米管复合电极超大容量电容器及其制造方法

本发明涉及一种碳纳米管复合电极超大容量电容器及其制造方法,所属领域为纳米技术及储能领域。

超大容量电容器是一种介于蓄电池与传统介质电容器之间的新型储能器件,传统介质电容器是通过电介质的极化来储存电荷,而超大容量电容器是通过电解质离子与电极的相互作用来储存电荷。与传统介质电容器相比,它具有很高的比电容量,可存储的能量密度为传统介质电容器的10倍以上;与蓄电池相比,其功率密度高10倍以上,具有瞬间释放特大电流的特性并且充电效率很高、循环使用寿命长。

超大容量电容器可作为电动车辆驱动电源的功率单元,解决电动车发展中的“瓶颈”,以蓄电池加超大容量电容器的复合动力源电动车辆,蓄电池提供正常运行状态下所需平均功率,而在爬坡、启动、制动状态下所需加速功率由并联的超大容量电容器提供,超大容量电容器作为“峰值功率单元”,可有效地减轻蓄电池的峰值功率压力,使蓄电池每次充电的持续里程增大数倍,使蓄电池的循环使用寿命延长。超大容量电容器也可应用于军事方面,如微波武器、激光武器提供MW级的特大启动功率;还可用作电子设备中的备用电源,如电视机、摄录像机、个人电脑、移动电话机的不间断供电系统;可用于工业设备的闪光、点火装置,如照相机、电焊机、充磁机、X光机、燃料电池的引发电源。

超大容量电容器形成电容的方式有双电层电容和赝电容两种,双电层电容是在电极/电解质界面通过电子和离子的定向排列造成电荷的对峙所产生。赝电容是在电极表面或体相中的二维或准二维空间上,电活性物质发生高度可逆的氧化还原反应或吸附脱附过程,从而实现电荷的储存和释放并形成电容。赝电容方式形成的比电容量可达双电层电容的10倍以上。与上面两种电容方式对应的器件即双电层电容器和赝电容器。

通常双电层电容器主要以高比表面积活性炭、活性炭纤维、碳气凝胶等作为电极材料,但这些材料导电性较差,所得电容器等效串联电阻大;另外,活性炭中有大量孔径为 2nm 或更小的微孔,电解质离子难以进入这些孔中,因此其比表面积利用率低;并且结构上存在所谓的“死孔”,这使得其频率响应特性差。近年来,由于碳纳米管的发现,应用碳纳米管作为超大容量电容器电极材料已引起研究者的重视,碳纳米管是由单层或多层石墨面卷曲而成的中空纳米级管状材料。在一定的形状和尺寸条件下,碳纳米管具有良好的导电性;碳纳米管相互交织缠绕形成网状结构,网孔尺寸主要分布在 2-50 nm 之间,具有巨大的有效比表面积,适合双电层电容的形成;碳纳米管三维网络的网孔之间相互贯通,没有活性炭结构上的所谓“死孔”。但碳纳米管主要是形成双电层电容,比电容量相对较小,约为 100 F/g (按单电极活性物质计算)。如:马仁志,魏秉庆,徐才录,等在《中国科学》杂志上(E 辑,2000,30(2):112-116)发表的《基于碳纳米管的超级电容器》。

而赝电容器常以金属氧化物  $\text{RuO}_2$  为电极材料, $\text{RuO}_2$  导电率高,所得超大容量电容器的比电容量高,但是  $\text{RuO}_2$  价格昂贵,寻找廉价的替代  $\text{RuO}_2$  的电极材料引起研究者的兴趣。如:王晓峰等等在《电源技术》杂志上(2001,25(3))发表的《氧化镍超电容器的研究》。用镍的氧化物( $\text{NiO}$ )为电极材料,但镍的氧化物( $\text{NiO}$ )导电性较差,所得超大容量电容器的等效串联电阻大。另外,过渡金属氧化物的成型性能差。另一类赝电容器电极材料是导电聚合物,包括聚苯胺(PAN)及其衍生物、聚噻吩(PTH)及其衍生物、聚吡咯(PPY)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物;基于导电聚合物的超大容量电容器可以形成赝电容从而获得较大的比电容量,但导电聚合物的导电性也差。另外,导电聚合物的机械强度低。

电极材料决定超大容量电容器的性能,上面提到的电极材料中碳纳米管能达到较高的电导率,但它主要是形成双电层电容,比电容量相对较小。而过渡金

属氧化物和导电聚合物可形成赅电容，获得较高的比电容量，但导电性较差。这意味着目前的超大容量电容器电极材料在高比电容量与高电导率方面难以兼顾。另外，过渡金属氧化物成型性能差，导电聚合物机械强度低，这都将影响超大容量电容器的性能。

付旭涛等人申请的《掺碳纳米管超大容量电容器》，专利申请号为：00136008.6的发明专利将活性炭（或活性炭纤维）与碳纳米管复合，作为超大容量电容器电极材料，但这种材料中无过渡金属氧化物或导电聚合物，难以形成赅电容，所得的比电容小。李永熙等人申请的《使用新材料的电极的超级电容器以及制造方法》，专利申请号为：01109703.5的发明专利用碳纳米管或镀镍碳纳米管作为超大容量离子电容器电极材料，但这种材料中无过渡金属氧化物或导电聚合物，难以形成赅电容；另外，这种材料成本太高。而解晶莹等人申请的《电化学超电容器以及制造方法》，专利申请号为：00119499.2的发明专利以镍的氧化物或氢氧化物为超大容量离子电容器的正极材料，以多孔大面积炭为负极材料，但镍的氧化物或氢氧化物的导电性差，所得超大容量电容器的等效串联电阻大。

本发明专利的目的是为了获得同时能形成高比电容量、具有良好的导电性、具有良好的成型性能和机械性能的超大容量电容器电极材料及由此制得的电极，进而制得比电容量高、等效串联电阻低的超大容量电容器。

本发明专利的原理是：拟采用碳纳米管与过渡金属氧化物与（或）导电聚合物相复合的途经，在所得复合电极中碳纳米管具有良好的导电性，而过渡金属氧化物和导电聚合物可形成较高的比电容量。碳纳米管在复合电极中形成网状结构，成为导电性良好的电荷通路；而过渡金属氧化物、导电聚合物能形成赅电容、得到较高的比电容量，这使得超大容量电容器电极既能形成高比电容量、又具有高电导率。另外，在碳纳米管复合电极材料中，碳纳米管本身的比表面积大，可以形成较大的双电层容量；在复合材料的制备过程中，碳纳米管

可以作为过渡金属氧化物、导电聚合物的形核基底，有利于得到晶粒细小的过渡金属氧化物、导电聚合物；并且，碳纳米管与过渡金属氧化物、导电聚合物的机械性能互补，如过渡金属氧化物可依附在碳纳米管网络上，从而得到较好的成型性能；导电聚合物的机械强度较差，导电聚合物与碳纳米管复合后将使其机械强度明显提高。而成型性能和机械强度对电极材料来说也是很重要的。

本发明专利的关键技术问题的技术方案是这样实现的：本发明专利采用将导电性良好的碳纳米管与涉及到的其它导电性较差的过渡金属氧化物、导电聚合物系列、活性炭系列相复合的方法，从而得到同时能形成高比电容量和具有良好的导电性的超大容量电容器电极材料。具体的复合方案有如下6种：

- (1) 碳纳米管与过渡金属氧化物复合，这一复合材料中碳纳米管的重量百分比为10%-90%，过渡金属氧化物的重量百分比为90%-10%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )。
- (2) 碳纳米管与导电聚合物系列复合，这一复合材料中碳纳米管的重量百分比为10%-90%，导电聚合物的重量百分比为90%-10%。这里的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物。
- (3) 碳纳米管与过渡金属氧化物、导电聚合物同时复合，这一复合材料中碳纳米管的重量百分比为10%-90%，过渡金属氧化物的重量百分比为50%-5%，导电聚合物的重量百分比为40%-5%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )；这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物。
- (4) 碳纳米管与过渡金属氧化物、活性炭系列同时复合，这一复合材料中碳纳米管的重量百分比为10%-90%，过渡金属氧化物的重量百分

比为 50%-5%，活性炭系列的重量百分比为 40%-5%。这里所指的过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )；这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。

- (5) 碳纳米管与导电聚合物系列、活性炭系列同时复合，这一复合材料中碳纳米管的重量百分比为 10%-90%，导电聚合物的重量百分比为 50%-5%，活性炭系列的重量百分比为 40%-5%。这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物；这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。
- (6) 碳纳米管与过渡金属氧化物、导电聚合物、活性炭系列同时复合，这一复合材料中碳纳米管的重量百分比为 10%-90%，过渡金属氧化物的重量百分比为 30%-3%，导电聚合物的重量百分比为 30%-5%，活性炭系列的重量百分比为 30%-2%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )；这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物；这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。

上述 6 种复合方案中所提到的碳纳米管在复合前需进行氧化处理，氧化处理在空气或液体介质中进行，氧化处理温度为 80-120℃，氧化处理时间为 2-10 小时。上述方案中提到的过渡金属氧化物中可以掺入稀土元素 Ce 或 La；也可以不掺 Ce 或 La。然后按复合方案配料，进行充分研磨，再在其中加入重量百分比为 1%-20%的粘结剂，粘结剂包括聚四氟乙烯乳液、羧甲基纤维素、聚乙烯

醇。用搅拌均匀的复合电极材料压制在泡沫镍、石墨片、镍片、铝片或铜片上，制成一定形状的复合电极。压制方法包括普通模压法、冷等静压法、热等静压法。两个相同的碳纳米管复合电极用一电解质离子可以通过的隔膜分隔，隔膜为玻璃纤维纸或聚合物膜。然后装入外壳中，再注入电解质溶液，电解质溶液可用氢氧化钠水溶液、氢氧化钾水溶液、氢氧化锂水溶液、硫酸水溶液、硝酸水溶液、高氯酸锂的碳酸丙烯酯溶液、四氟硼酸四乙基铵的碳酸丙烯酯溶液，或其混合液。封装后即得超大容量电容器。

实施例：本发明涉及现有的超大容量电容器电极材料可分成两类，一类是导电性良好的碳纳米管，另一类是导电性较差的过渡金属氧化物、活性炭系列和导电聚合物系列。本发明采用将导电性良好的碳纳米管与涉及到的其它导电性较差的过渡金属氧化物、活性炭系列、导电聚合物系列相复合的办法，从而得到同时能形成高比电容量和具有良好的导电性的超大容量电容器电极材料。

具体的复合方案有如下6种：

- (1) 碳纳米管与过渡金属氧化物复合，这一复合材料中碳纳米管的重量百分比为10%-90%，过渡金属氧化物的重量百分比为90%-10%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )。
- (2) 碳纳米管与导电聚合物系列复合，这一复合材料中碳纳米管的重量百分比为10%-90%，导电聚合物的重量百分比为90%-10%。这里的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物。
- (3) 碳纳米管与过渡金属氧化物、导电聚合物同时复合，这一复合材料中碳纳米管的重量百分比为10%-90%，过渡金属氧化物的重量百分比为50%-5%，导电聚合物的重量百分比为40%-5%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ )；这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、



聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物。

- (4) 碳纳米管与过渡金属氧化物、活性炭系列同时复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,过渡金属氧化物的重量百分比为 50%-5%,活性炭系列的重量百分比为 40%-5%。这里所指的过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ );这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。
- (5) 碳纳米管与导电聚合物系列、活性炭系列同时复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,导电聚合物的重量百分比为 50%-5%,活性炭系列的重量百分比为 40%-5%。这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物;这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。
- (6) 碳纳米管与过渡金属氧化物、导电聚合物、活性炭系列同时复合,这一复合材料中碳纳米管的重量百分比为 10%-90%,过渡金属氧化物的重量百分比为 30%-3%,导电聚合物的重量百分比为 30%-5%,活性炭系列的重量百分比为 30%-2%。这里所指过渡金属氧化物包括镍的氧化物( $\text{NiO}_x$ )、钴的氧化物( $\text{CoO}_x$ );这里所指的导电聚合物系列包括聚苯胺(PAN)及其衍生物、聚吡咯(PPY)及其衍生物、聚噻吩(PTH)及其衍生物、聚对苯(PPP)及其衍生物、聚并苯(PAS)及其衍生物;这里所指的活性炭系列包括活性炭、活性炭纤维、活性炭纤维布以及碳气凝胶。

上述 6 种复合方案中所提到的碳纳米管在复合前需进行氧化处理,氧化处理在空气或液体介质中进行,氧化处理温度为 80-120℃,氧化处理时间为 2-10

小时。上述方案中提到的过渡金属氧化物中可以掺入稀土元素 Ce 或 La；也可以不掺 Ce 或 La。然后按复合方案配料，进行充分研磨，再在其中加入重量百分比为 1%-20%的粘结剂，粘结剂包括聚四氟乙烯乳液、羧甲基纤维素、聚乙烯醇。用搅拌均匀的复合电极材料压制在泡沫镍、石墨片、镍片、铝片或铜片上，制成一定形状的复合电极。压制方法包括普通模压法、冷等静压法、热等静压法。两个相同的碳纳米管复合电极用一电解质离子可以通过的隔膜分隔，隔膜为玻璃纤维纸或聚合物膜。然后装入外壳中，再注入电解质溶液，电解质溶液可用氢氧化钠水溶液、氢氧化钾水溶液、氢氧化锂水溶液、硫酸水溶液、硝酸水溶液、高氯酸锂的碳酸丙烯酯溶液、四氟硼酸四乙基铵的碳酸丙烯酯溶液或其混合液。封装后即得超大容量电容器。

本发明专利的优点是：上述复合电极中的碳纳米管能形成导电性良好的导电网络，而其中过渡金属氧化物、导电聚合物系列能形成大的比电容量。从而，得到同时能形成高比电容量和具有良好的导电性的超大容量电容器电极材料。另外，在碳纳米管复合电极材料中，碳纳米管本身的比表面积大，可以形成较大的双电层容量；在复合材料的制备过程中，碳纳米管可以作为过渡金属氧化物、导电聚合物的形核基底，有利于得到晶粒细小的过渡金属氧化物、导电聚合物；并且，碳纳米管与过渡金属氧化物、导电聚合物的机械性能互补，如过渡金属氧化物可依附碳纳米管网络，可得到较好的成型性能；导电聚合物的机械强度较差，导电聚合物与碳纳米管复合后将使其机械强度明显提高；而活性炭系列的添加可以降低成本。本专利的应用意味着新型超大容量电容器电极材料的出现，将推进超大容量电容器的应用和研究进程，产生较大的经济和社会效益。通过本发明的实施，可以得到同时能形成高比电容量和具有良好的导电性、具有较好的成型性能和机械强度的超大容量电容器电极材料，运用该电极材料可生产出超大容量电容器。